

Transition moments between excited electronic states from the Hermitian formulation of the coupled cluster quadratic response function

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We introduce a new method for the computation of the transition moments between the excited electronic states based on the expectation value formalism of the coupled cluster theory [B. Jeziorski and R. Moszynski, *Int. J. Quant. Chem.* **48**, 161 (1993)]. The working expressions of the new method solely employ the coupled cluster amplitudes. In the approximation adopted in the present paper the cluster expansion is limited to single, double, and linear triple excitations. The computed dipole transition probabilities for the singlet-singlet and triplet-triplet transitions in alkali earth atoms agree well with the available theoretical and experimental data. In contrast to the existing coupled cluster response theory, the matrix elements obtained by using our approach satisfy the Hermitian symmetry even if the excitations in the cluster operator are truncated. As a part of the numerical evidence for the new method, we report calculations of the transition moments between the excited triplet states which have not yet been reported in the literature within the coupled cluster theory. Slater-type basis sets constructed according to the correlation-consistency principle are used in our calculations.

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I. INTRODUCTION

Response of a system to external perturbations is described by linear, quadratic, and higher-order response functions.¹⁻³ Many physical observables such as transition probabilities, dynamic polarizabilities, hyperpolarizabilities, and lifetimes are defined through the response functions or can be derived from the response functions. Until recently, properties of the excited electronic states were not easily available in high-resolution experiments, but with the advances of new spectroscopic techniques in the hot pipe⁴⁻⁷ and ultracold experiments,⁸⁻¹² more and more accurate experimental data become available and possibly need theoretical interpretation. Theoretical information about the transition moments between the excited states is also necessary to propose new routes to obtain molecules in the ground rovibrational state (see, e.g., Ref. 13). Last but not least, excited states properties define the asymptotics of the excited state interaction potentials,¹⁴ and play an unexpectedly important role in the dynamics of nuclear motions in the presence of external fields.¹⁵

The properties of the excited states, e.g., polarizabilities, transition strengths, and lifetimes can be obtained from limited multiconfiguration interaction theory, but this approach inherently suffers from the size inconsistency problem. Applying the size consistent coupled cluster (CC) formalism to the response function opens up a possibility of an accurate description of molecular properties with an affordable computational cost for medium size molecules. In the 1990s Jørgensen and collaborators formulated the CC response theory,^{16,17} based on the coupled cluster generalization of the Hellmann-Feynman theorem where the average value is replaced by a transition expectation value with respect to the coupled cluster state. However, in this theory the necessary Hermiticity condition required from the transition moments is not satisfied, and in some cases this leads to unphysical numerical results.

In the present study we focus on the molecular properties that can be obtained from the quadratic response function, $\langle\langle X; Y, Z \rangle\rangle_{\omega_Y, \omega_Z}$. The latter describes the response of an observable X to perturbations Y and Z oscillating with the frequencies ω_Y and ω_Z , respectively. The transition moment \mathcal{T}_{LM}^X between the excited states is computed from the double residue of the quadratic response function

$$\lim_{\omega_Y \rightarrow -\omega_L} (\omega_L + \omega_Y) \lim_{\omega_Z \rightarrow \omega_M} (\omega_M - \omega_Z) \langle\langle X; Y, Z \rangle\rangle_{\omega_Y, \omega_Z} = \mathcal{T}_{0L}^Y (\mathcal{T}_{LM}^X - \delta_{LM} \langle \Psi_0 | X | \Psi_0 \rangle) \mathcal{T}_{M0}^Z, \quad (1)$$

where \mathcal{T}_{0L}^Y and \mathcal{T}_{M0}^Z are transition moments between the ground and excited states, and ω_K is the excitation energy of the state K . The transition moments are necessary to compute the transition probabilities¹⁸

$$A_{LM} = \frac{1}{3} \frac{16\pi^3}{h\epsilon_0\lambda^3} \mathcal{S}_{LM}, \quad (2)$$

where ϵ_0 is the vacuum permittivity, λ is the wavelength, h is the Planck constant, and the transition strength \mathcal{S}_{LM} is defined as

$$\mathcal{S}_{LM} = |\mathcal{T}_{LM}|^2. \quad (3)$$

The lifetime¹⁸ of a state L is defined as

$$\tau_L = \frac{1}{\sum_K A_{LK}}. \quad (4)$$

There exists two coupled cluster approaches for the computation of the transition moments between the ground and excited states, the linear response coupled cluster theory (LRCC) of Koch et al.^{16,17,19,20} and the coupled cluster expectation value formulation of the linear response function (XCC) of Tucholska et al.²¹ As already stated above, for the transition moments between the excited states, the only available approach is based on the quadratic response coupled cluster (QRCC) theory of Koch et al.^{16,17,19,20} In the present work we generalize the approach of Refs. 22 and 21 to the calculation of transition properties between the excited states. The transition moments, \mathcal{T}_{LM}^X , where L and M denote the singlet or triplet excited states, are extracted from the response function to compute lifetimes and transition probabilities.

In the exact theory, the transition moments are Hermitian

$$\mathcal{T}_{LM}^X = (\mathcal{T}_{ML}^X)^*, \quad (5)$$

but this relation is violated by the existing QRCC method, in some cases to a large degree, when the cluster operator is truncated at some excitation level. In extreme cases this leads to non-physical, negative transition strengths which will be discussed in detail in the remaining part of this work. Recently, a new approach to the problem has been proposed, where molecular properties are computed as derivatives of the eigenvalues of a Hermitian

eigenproblem.²³ This approach should apparently remove the inaccuracies and inconsistencies of the QRCC theory. However, numerical results for this method are not yet available and we cannot assess its accuracy. Therefore, we will restrict our comparisons to the original QRCC theory.

This paper is organized as follows. In sections II A and II B we derive the formula for the XCC transition moments between the excited states. In section II C we present the truncations and approximations used in this work. In section III we report numerical results for the transition moments and lifetimes of the Mg and Sr atoms, and for the Mg₂ molecule. First, we present the comparison of our results with the QRCC method (subsection III B), next we compare our results with the available theoretical and experimental data (subsection III C) and finally, we investigate the Hermiticity violation in the XCC and QRCC methods (subsection III D). In section IV we conclude our paper.

II. THEORY

A. Basic definitions

In the CC theory the ground state wave function Ψ_0 is represented by the exponential Ansatz $\Psi_0 = e^T \Phi$, where the cluster operator T is given by the sum of n -tuple excitation operators T_n ,

$$T = \sum_{n=1}^N T_n, \quad (6)$$

$$T_n = \frac{1}{n!} \sum_{\mu_n} t_{\mu_n} \mu_n, \quad (7)$$

$\mu_n = E_{ai} E_{bj} \cdots E_{fm}$ is the product of spin-free excitation operators, Φ is the Slater determinant built of the occupied orbitals, and N is the number of electrons. Throughout the work, the indices $a, b, c \dots$ and $i, j, k \dots$ denote virtual and occupied orbitals, respectively, and $p, q, r \dots$ are used in summations over all orbitals. In practical applications the operator T is truncated to make the CC calculation computationally feasible.

The expectation value of an observable X in the XCC theory is given by the explicitly

connected, size-consistent expression introduced by Jeziorski and Moszynski²⁴

$$\frac{\langle e^T \Phi | X | e^T \Phi \rangle}{\langle e^T \Phi | e^T \Phi \rangle} = \langle \Phi | e^{S^\dagger} e^{-T} X e^T e^{-S^\dagger} \Phi \rangle. \quad (8)$$

The auxiliary operator S is defined as

$$|e^S \Phi\rangle = \frac{|e^T e^{T^\dagger} \Phi\rangle}{\langle e^T \Phi | e^T \Phi \rangle}, \quad S = S_1 + S_2 + \dots + S_N, \quad (9)$$

and S_n is expressed as²⁴

$$\begin{aligned} S_n = T_n - \frac{1}{n} \hat{\mathcal{P}}_n \left(\sum_{k=1} \frac{1}{k!} [\tilde{T}^\dagger, T]_k \right) \\ - \frac{1}{n} \hat{\mathcal{P}}_n \left(\sum_{k=1} \sum_{m=0} \frac{1}{k!} \frac{1}{m!} [[\tilde{S}, T^\dagger]_k, T]_m \right), \end{aligned} \quad (10)$$

where

$$\tilde{T} = \sum_{n=1}^N n T_n, \quad \tilde{S} = \sum_{n=1}^N n S_n, \quad (11)$$

and $[A, B]_k$ is a k -tuply nested commutator. The superoperator $\hat{\mathcal{P}}_n(X)$ yields the n -tuple excitation part of X

$$\hat{\mathcal{P}}_n(X) = \frac{1}{n!} \sum_{\mu_n} \langle \tilde{\mu}_n | X \rangle \mu_n, \quad (12)$$

where for simplicity we introduce the following notation $\langle A | B \rangle = \langle A \Phi | B \Phi \rangle$

The formula for S is a finite expansion, though it contains terms of high order in the fluctuation potential.²⁴ To find the exact S operator one requires an iterative procedure. However, S can efficiently be approximated while retaining the size-consistency. In our previous work,²¹ we presented a hierarchy of approximations and assessed their accuracy. Let $S_n(m)$ denote the n -electron part of S , where all available contributions up to the order m in the fluctuation potential are accounted for. In the computations based on the CC3

model (single, double, and linear triple excitations), we employ

$$\begin{aligned}
S_1(3) &= T_1 + \hat{\mathcal{P}}_1 \left([T_1^\dagger, T_2] \right), \\
&\quad + \hat{\mathcal{P}}_1 \left([T_2^\dagger, T_3] \right), \\
S_2(3) &= T_2 + \frac{1}{2} \hat{\mathcal{P}}_2 \left([[T_2^\dagger, T_2], T_2] \right), \\
S_3(2) &= T_3,
\end{aligned} \tag{13}$$

where the CC3 equations for T_1 , T_2 and T_3 are given by Koch et al.²⁵ In the instances where the underlying model of the wave function is CCSD, we employ $S = S_1(3) + S_2(3)$ neglecting the terms including T_3 .

The exact quadratic response function can be written as the sum over states

$$\langle\langle X; Y, Z \rangle\rangle_{\omega_Y, \omega_Z} = P_{XYZ} \sum_{\substack{K=1 \\ N=1}} \frac{\langle \Psi_0 | Y | K \rangle \langle K | X - \langle \Psi_0 | X | \Psi_0 \rangle | N \rangle \langle N | Z | \Psi_0 \rangle}{(\omega_K + \omega_Y)(\omega_N - \omega_Z)}, \tag{14}$$

where K and N run over all possible excitations, and $|\Psi_0\rangle$ is the ground state. The action of the permutation operator P_{XYZ} yields six distinct contributions to $\langle\langle X; Y, Z \rangle\rangle_{\omega_Y, \omega_Z}$ with the indices X , Y , and Z being interchanged.

B. XCC transition moments

The exact transition moment between the excited states L and M can be identified from the double residue of the quadratic response function²⁰

$$\begin{aligned}
&\lim_{\omega_Y \rightarrow -\omega_L} (\omega_L + \omega_Y) \lim_{\omega_Z \rightarrow \omega_M} (\omega_M - \omega_Z) \langle\langle X; Y, Z \rangle\rangle_{\omega_Y, \omega_Z} \\
&= \langle \Psi_0 | Y | L \rangle \langle L | X - \langle \Psi_0 | X | \Psi_0 \rangle | M \rangle \langle M | Z | \Psi_0 \rangle = \mathcal{T}_{0L}^Y \mathcal{T}_{LM}^X \mathcal{T}_{M0}^Z.
\end{aligned} \tag{15}$$

To obtain \mathcal{T}_{LM}^X we express $\langle\langle X; Y, Z \rangle\rangle_{\omega_Y, \omega_Z}$ by using the XCC formalism and take the limit of Eq. (15).

Let us introduce the coupled cluster parametrization of the quadratic response function. Using the fact that the first order wave function $\Psi^{(1)}(\omega)$ is expressible through the resolvent \mathcal{R}_ω ,

$$\Psi^{(1)}(\omega_V) = \mathcal{R}_\omega V |\Psi_0\rangle, \quad V = Y \text{ or } Z \tag{16}$$

$$\mathcal{R}_\omega = \sum_{N=1} \frac{|N\rangle\langle N|}{\omega_N + \omega}, \quad (17)$$

the expression for the quadratic response function, Eq. (14), can be reformulated as follows

$$\langle\langle X; Y, Z \rangle\rangle_{\omega_Y, \omega_Z} = P_{XYZ} \langle \Psi^{(1)}(\omega_Y) | X_0 | \Psi^{(1)}(-\omega_Z) \rangle, \quad (18)$$

where $X_0 = X - \langle X \rangle$ and $\langle X \rangle = \langle \Psi_0 | X | \Psi_0 \rangle$. The normalized ground state wave function in the coupled cluster parametrization is given by

$$|\Psi_0\rangle = \frac{|e^T \Phi\rangle}{\langle e^T \Phi | e^T \Phi \rangle^{\frac{1}{2}}}. \quad (19)$$

The CC first order wave function $\Psi^{(1)}(\omega)$ is given by the operator $\Omega(\omega)$ acting on the normalized ground state,²²

$$|\Psi^{(1)}(\omega)\rangle = (\Omega_0 + \Omega(\omega)) \frac{|e^T \Phi\rangle}{\langle e^T \Phi | e^T \Phi \rangle^{\frac{1}{2}}}. \quad (20)$$

We choose $\Omega_0 = -\langle \Psi_0 | \Omega(\omega) | \Psi_0 \rangle$ to ensure the orthogonality of $\Psi^{(1)}$ to Ψ_0 . The excitation operator $\Omega(\omega)$ is the solution of the linear response equation^{22,26}

$$\langle \mu | [e^{-T} H e^T, \Omega(\omega)] + \omega \Omega(\omega) + e^{-T} X e^T \rangle = 0. \quad (21)$$

Let us define

$$\alpha(X; Y, Z) = \langle \Psi^{(1)}(\omega_Y) | X_0 | \Psi^{(1)}(-\omega_Z) \rangle. \quad (22)$$

By inserting Eq. (20) into Eq. (22) we arrive at

$$\begin{aligned}
\alpha(X; Y, Z) = & \langle (\Omega_0^Y + \Omega^Y(\omega_Y)) \Psi_0 | X_0 | (\Omega_0^Z + \Omega^Z(-\omega_Z)) \Psi_0 \rangle = \\
& \frac{\langle \Omega^Y(\omega_Y) e^T | e^T \rangle \langle e^T | \Omega^Z(-\omega_Z) e^T \rangle \langle e^T | X_0 | e^T \rangle}{\langle e^T | e^T \rangle \langle e^T | e^T \rangle \langle e^T | e^T \rangle} \\
& - \frac{\langle \Omega^Y(\omega_Y) e^T | e^T \rangle \langle e^T | X_0 | \Omega^Z(-\omega_Z) e^T \rangle}{\langle e^T | e^T \rangle \langle e^T | e^T \rangle} \\
& - \frac{\langle e^T | \Omega^Z(-\omega_Z) e^T \rangle \langle \Omega^Y(\omega_Y) e^T | X_0 | e^T \rangle}{\langle e^T | e^T \rangle \langle e^T | e^T \rangle} \\
& + \frac{\langle \Omega^Y(\omega_Y) e^T | X_0 | \Omega^Z(-\omega_Z) e^T \rangle}{\langle e^T | e^T \rangle}, \tag{23}
\end{aligned}$$

where $\Omega^V(\omega_V)$ is solution of Eq. (21) with $X = V$ and $\omega = \omega_V$. Further algebraic manipulations are carried out by using the following identities

$$[e^T, \Omega] = 0, \tag{24}$$

$$e^{-S^\dagger} \Phi = \Phi, \tag{25}$$

$$X \Phi = \langle X \rangle \Phi + \hat{\mathcal{P}}(X) \Phi, \tag{26}$$

$$\frac{\langle e^T | X | e^T \rangle}{\langle e^T | e^T \rangle} = \langle e^{S^\dagger} e^{-T} X e^T e^{-S^\dagger} \rangle, \tag{27}$$

so that the final expression for $\alpha(X; Y, Z)$ in the XCC formulation reads

$$\alpha(X; Y, Z) = \left\langle \hat{\mathcal{P}}(e^{-S} e^{T^\dagger} \Omega^Y(\omega_Y) e^{-T^\dagger} e^S) \middle| e^{S^\dagger} e^{-T} (X_0) e^T e^{-S^\dagger} \hat{\mathcal{P}}(e^{-S^\dagger} \Omega^Z(-\omega_Z) e^{S^\dagger}) \right\rangle. \tag{28}$$

We express the excitation operator $\Omega(\omega)$ in the basis of the right eigenvectors of the Jacobian matrix

$$\Omega(\omega) = \sum_N (O_N^Y(\omega_Y)) r_N, \tag{29}$$

where the CC Jacobian matrix is defined as

$$A_{\mu\nu} = \langle \tilde{\mu} | [e^{-T} H e^T, \nu] \rangle, \quad (30)$$

and

$$\langle \tilde{\mu} | \nu \rangle = \delta_{\mu\nu}. \quad (31)$$

For the single and double excitation manifold we use the biorthonormal basis proposed by Helgaker, Jørgensen, and Olsen,²⁷ and for the triply excited manifold we employ the basis proposed by Tucholska et al.²¹ We obtain the coefficients $O_N^Y(\omega)$ by projecting Eq. (21) onto the left eigenvector l_N of the Jacobian

$$O_N^Y(\omega_Y) = -\frac{\langle l_N | e^{-T} Y e^T \rangle}{\omega_N + \omega_Y}. \quad (32)$$

Therefore, by using the eigenvectors and eigenvalues of the CC Jacobian one can express $\alpha(X; Y, Z)$ as follows

$$\begin{aligned} \alpha(X; Y, Z) &= \sum_{\substack{K=1 \\ N=1}} \left(O_K^Y(\omega_Y) \right)^* O_N^Z(\omega_Z) \langle \kappa(r_K) | e^{S^\dagger} e^{-T} X_0 e^T e^{-S^\dagger} | \eta(r_N) \rangle \\ &= \sum_{\substack{K=1 \\ N=1}} \frac{\langle e^{-T} Y e^T | l_K \rangle}{\omega_K + \omega_Y} \frac{\langle l_N | e^{-T} Z e^T \rangle}{\omega_Z - \omega_N} \langle \kappa(r_K) | e^{S^\dagger} e^{-T} X_0 e^T e^{-S^\dagger} | \eta(r_N) \rangle, \end{aligned} \quad (33)$$

where

$$\begin{aligned} \kappa(r_N) &= \hat{\mathcal{P}} \left(e^{-S} e^{T^\dagger} r_N e^{-T^\dagger} e^S \right), \\ \eta(r_N) &= \hat{\mathcal{P}} \left(e^{S^\dagger} r_N e^{-S^\dagger} \right). \end{aligned} \quad (34)$$

Finally, the double residue from the quadratic response function is given by

$$\begin{aligned} \mathcal{T}_{0L}^Y \mathcal{T}_{LM}^X \mathcal{T}_{M0}^Z &= \lim_{\omega_Y \rightarrow -\omega_L} (\omega_L + \omega_Y) \lim_{\omega_Z \rightarrow \omega_K} (\omega_K - \omega_Z) \langle \langle X; Y, Z \rangle \rangle_{\omega_Y, \omega_Z} \\ &= \langle e^{-T} Y e^T | l_L \rangle \langle \kappa(r_L) | e^{S^\dagger} e^{-T} X_0 e^T e^{-S^\dagger} | \eta(r_M) \rangle \langle l_M | e^{-T} Z e^T \rangle. \end{aligned} \quad (35)$$

In order to gain access to the individual transition moment \mathcal{T}_{LM}^X we need to divide Eq. (35) by $\mathcal{T}_{0L}^Y \mathcal{T}_{M0}^Z$. As in the XCC theory we do not have access to \mathcal{T}_{0L}^Y and \mathcal{T}_{M0}^Z separately, we

define an auxiliary quantity

$$\chi_L^Y = \langle e^{-T} Y e^T | l_L \rangle \langle \kappa(r_L) | \eta(r_L) \rangle \langle l_L | e^{-T} Y e^T \rangle \quad (36)$$

which in the exact case is equal to $|\mathcal{T}_{0L}^Y|^2$. This quantity is then used to extract \mathcal{T}_{LM}^X from the double residue of the quadratic response function

$$\begin{aligned} \mathcal{T}_{LM}^X &= \pm \frac{\langle 0 | Y | L \rangle \langle L | X_0 | M \rangle \langle M | Z | 0 \rangle}{\sqrt{\langle 0 | Y | L \rangle \langle L | L \rangle \langle L | Y | 0 \rangle \langle 0 | Z | M \rangle \langle M | M \rangle \langle M | Z | 0 \rangle}} \\ &= \pm \frac{\lim_{\omega_Y \rightarrow -\omega_L} (\omega_L + \omega_Y) \lim_{\omega_Z \rightarrow \omega_M} (\omega_M - \omega_Z) \langle \langle X; Y, Z \rangle \rangle_{\omega_Y, \omega_Z}}{\sqrt{\chi_L^Y \chi_M^Z}}. \end{aligned} \quad (37)$$

The \pm sign results from taking the square root of $|\mathcal{T}_{0L}^Y|^2$. This fact is of no concern as both \mathcal{T}_{LM}^X and \mathcal{T}_{ML}^X have identical denominators and we compute the transition strengths which are products $\mathcal{T}_{LM}^X \mathcal{T}_{ML}^X$.

The final expression for \mathcal{T}_{LM}^X in the XCC theory is given by

$$\begin{aligned} \mathcal{T}_{LM}^X &= \pm \frac{\xi_L^Y \langle \kappa(r_L) | e^{S^\dagger} e^{-T} X_0 e^T e^{-S^\dagger} \eta(r_M) \rangle \xi_M^Z}{\sqrt{\xi_L^Y \langle \kappa(r_L) | \eta(r_L) \rangle (\xi_L^Y)^* \xi_M^Z \langle \kappa(r_M) | \eta(r_M) \rangle (\xi_M^Z)^*}} \\ &= \pm \frac{\langle \kappa(r_L) | e^{S^\dagger} e^{-T} X_0 e^T e^{-S^\dagger} \eta(r_M) \rangle}{\sqrt{\langle \kappa(r_L) | \eta(r_L) \rangle \langle \kappa(r_M) | \eta(r_M) \rangle}}, \end{aligned} \quad (38)$$

where

$$\xi_M^Z = \langle l_M | e^{-T} Z e^T \rangle. \quad (39)$$

Note that our formula for \mathcal{T}_{LM}^X is expressible solely in terms of commutators. Therefore, it is automatically size-consistent no matter the level of truncation of the T and S operators.

Alternatively, one can use the identities (24) — (27) to obtain the following expression for \mathcal{T}_{LM}^X :

$$\tilde{\mathcal{T}}_{LM}^X = \pm \frac{\langle \eta(r_L) | e^{S^\dagger} e^{-T} X_0 e^T e^{-S^\dagger} \kappa(r_M) \rangle}{\sqrt{\langle \kappa(r_L) | \eta(r_L) \rangle \langle \kappa(r_M) | \eta(r_M) \rangle}}. \quad (40)$$

It is easy to notice that as long as

$$\mathcal{T}_{LM}^X = \tilde{\mathcal{T}}_{LM}^X \quad (41)$$

the Hermiticity relation $\mathcal{T}_{LM}^X = (\mathcal{T}_{LM}^X)^*$ is satisfied. Eq. (41) is true for any truncated T

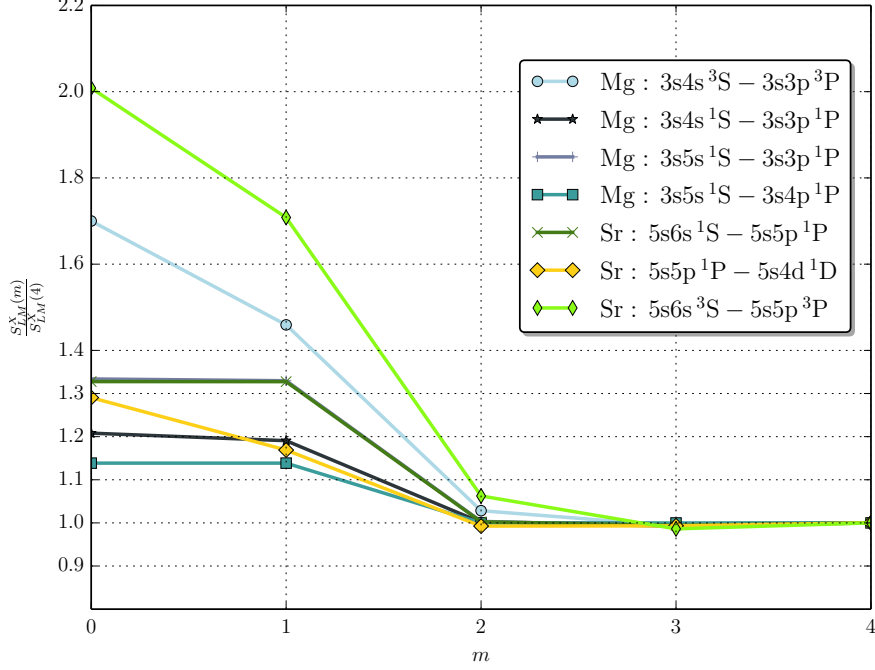


FIG. 1: Convergence of the XCC transition strengths with the MBPT order (m) for transition dipole strengths for Mg and Sr atoms. The T amplitudes are at the CC3/CCSD level of theory.

operator, and the exact S operator. This follows from the fact that in the derivation of the expression for \mathcal{T}_{LM}^X we used the definition from Eq. (9) which is valid only for the exact S operator.²⁴ Thus, the Hermiticity relation does not hold for an approximate S operator. However, the deviations from the exact symmetry are very small (see section III D).

C. Approximations

In order to obtain computationally tractable expressions for the transition moments we employ the approximate S operator defined by Eq. (13) and approximate coupled cluster amplitudes of the CCSD/CC3 theory. We must note that in practice one additional approximation is required to evaluate Eq. (38). We gather the terms in the commutator expansion into groups according to their leading-order in the many-body perturbation theory (MBPT). We ignore all terms which computational cost is higher than N^7 , with N being a measure of the system size. Including the terms accurate through the third-order in MBPT is sufficient to converge the transition strengths almost to the numerical limit, see Fig. (1). Therefore, throughout this work, we employ the third order approximation.

III. NUMERICAL RESULTS

A. Basis sets

Slater-type orbitals (STOs) used in this work were constructed according to the correlation-consistency principle,²⁸ similarly as by Lesiuk *et al.*²⁹ for the beryllium atom. The only difference in the procedure is that the exponents ζ were chosen according to the well-tempered formula, $(\zeta_{il} = \alpha_l + \beta_l i + \gamma_l i^2/n + \delta_l i^3/n^2)$, where n is the number of basis set functions for a given angular momentum, l . After some numerical experimentation, the value of δ_l was set equal to zero for $l > 2$. A detailed composition of the STOs basis sets is available from the authors upon request.

In Table I we demonstrate how the underlying coupled cluster approximation (CCSD/CC3) and the basis set (Gaussian/Slater) affect the calculated excitation energies for the magnesium atom. While including the connected triple amplitudes is important, the use of the Slater-type orbitals (STOs) yields a dramatic improvement in the accuracy of the excited states energies

TABLE I: Singlet and triplet energy levels (cm^{-1}) of the magnesium atom computed using Gaussian (G) and Slater (S) basis sets.

Level	E_{exp}	XCCSD(G) ^a	XCC3(G) ^a	XCCSD4(S) ^b	XCC34(S) ^b	XCCSD5(S) ^c	XCC35(S) ^c
3 p ¹ P ^o	35051	-246	-269	-13	-111	69	-87
4 s ¹ S	43503	-421	-413	-103	-115	37	-92
3 d ¹ D	46403	497	356	194	-132	241	121
4 p ¹ P ^o	49346	-394	-363	413	443	11	-56
5 s ¹ S	52556	-214	-186	-	-	261	168
3 p ³ P ^o	21891	-525	-	241	-	-292	-
4 s ³ S	41197	-447	-	118	-	-110	-
4 p ³ P ^o	47848	-399	-	10	-	-46	-
3 d ³ D	47957	1325	-	-	-	-85	-

^a Gaussian basis set: d-aug-cc-pVQZ^{30,31}

^b Slater basis set: mg-dawtcc4d basis of Lesiuk *et al.*^{29,32,33} with a similar number of basis function as the Gaussian basis set.

^c Slater basis set: mg-dawtcc5d basis of Lesiuk *et al.*^{29,32,33}

B. Comparison with the QRCC theory

Let us compare our results with the QRCC results obtained with the Dalton program package.³⁴ Although both methods originate from the coupled cluster theory, their working expressions are different and in general, they are not expected to give identical results. We computed the first few singlet-singlet transition moments for the Mg atom with both methods. The results are given in Table II. One can see a relatively good agreement between the two methods.

It is clear from Table II that the CC3 approximation has a little effect on the transition strength values. Yet we use the CC3 approximation as it gives better excitation energies, necessary for the lifetime computations. We also present the results obtained with the Slater orbitals to emphasize the influence of this basis on the computed transition strengths. It is worth noting that the use of the Slater orbitals leads in some cases to substantially different results.

TABLE II: Transition strengths \mathcal{S}_{LM}^X (a.u.) in the XCC and QRCC methods for the Mg atom.

Transition	XCCSD(G) ^a	XCC3(G) ^a	QRCCSD(G) ^a	QRCC3(G) ^a	XCCSD(S) ^b	XCC3(S) ^b
3s4s ¹ S - 3s3p ¹ P ^o	16.2	16.0	18.3	18.3	16.0	15.8
3s4p ¹ P ^o - 3s4s ¹ S	70.4	69.9	73.7	69.6	71.6	70.8
3s5s ¹ S - 3s4p ¹ P ^o	101.8	101.7	101.6	101.6	97.8	98.2
3s5s ¹ S - 3s3p ¹ P ^o	0.3	0.3	0.4	0.4	0.3	0.3
3s3d ¹ D - 3s3p ¹ P ^o	12.7	12.2	10.3	10.0	23.7	20.3
3s4p ¹ P ^o - 3s3d ¹ D	41.8	42.4	43.0	— [*]	86.2	79.6

^a Gaussian basis set: d-aug-cc-pVQZ^{30,31}

^b Slater basis set: mg-dawtcc5d basis of Lesiuk et al.^{29,32,33}

^{*} Non-physical value. For details see section III D.

C. Comparison with the available theoretical and experimental data

In Table III we present a comparison of our computed transition strengths with other theoretical approaches, the relativistic multiconfigurational Hartree Fock approximation (Fischer³⁵), the CI approximation with the *B*-spline basis (Chang and Tang³⁶), and the semi-empirical weakest bound electron potential model (Zheng et al.³⁷). The \mathcal{S}_{LM}^X values of Chang and Tang were derived from A_{LM}^X with the experimental excitation energies.

TABLE III: Transition strengths \mathcal{S}_{LM}^X (a.u.) for the Mg atom.

Transition	XCC3(G) ^a	XCC3(S) ^b	Chang	Fischer	Zheng
3s4s ¹ S - 3s3p ¹ P ^o	16.0	15.8	17.9	18.1	18.8
3s4p ¹ P ^o - 3s4s ¹ S	69.9	70.8	69.9	65.4	77.2
3s5s ¹ S - 3s4p ¹ P ^o	101.8	98.2	91.7	92.3	87.4
3s5s ¹ S - 3s3p ¹ P ^o	0.3	0.3	0.4	0.3	0.9
3s3d ¹ D - 3s3p ¹ P ^o	12.2	20.3	21.5	21.4	61.5
3s4p ¹ P ^o - 3s3d ¹ D	42.4	79.6	76.6	81.9	83.7

^a Gaussian basis set: d-aug-cc-pVQZ^{30,31}

^b Slater basis set: mg-dawtcc5d basis of Lesiuk et al.^{29,32,33}

The XCC3(S) results are in a much better agreement with the results calculated with other theoretical methods than the results obtained with the XCC3(G) and with QRCC3(G) methods. The most dramatic improvement is observed for the 3d¹D–3p¹P^o and 4p¹P^o–3d¹D transitions.

The combination of the XCC3 method and the STOs basis set results in lifetimes of the excited states of the Mg atom in a very good agreement with the available experimental and theoretical data (Tables IV and V). For the singlet states, we find an excellent agreement with the most recent experimental data,³⁸ but not with the older experiment of Schaefer.³⁹ Our results are consistent with the lifetimes computed by Froese³⁵ and Chang,³⁶ but they are in a significant disagreement with the semi-empirical values of Zheng.³⁷

All the computed lifetimes for the triplet states of Mg agree well with the existing experimental and theoretical results (Table V). Remarkably, the XCCSD(S) results are close to the most recent experimental data of Aldenius⁴² for all states where the data are available. For the 3s5s ³S state other theoretical results support the older values of Schaefer³⁹ and Gratton.³⁸ Similarly, in the case of the 3s4s ³S state, the lifetimes calculated at the XCCSD(S) level are slightly larger than the other theoretical results, yet in an excellent agreement with the Aldenius experiment.⁴² For the 3s4p ³P state there are no experimental results available, but all the theoretical lifetimes, including the XCCSD(S) one, are consistent within 10% at worst. The triplet-triplet transition dipole moments which are necessary to compute the lifetimes of the triplet states are not available in the QRCC implementation. Therefore, no comparison with the QRCC method is possible.

In Table VI we present transition probabilities for the Sr atom. For the singlet states we note a good agreement with the Werij⁵⁰ results. For the 5s5p¹P^o–5s4d¹D transition

TABLE IV: Lifetimes (in ns) of singlet excited states of the magnesium atom. Years of publication are given in parentheses.

Ref.	3s3p $1P^\circ$	3s4s $1S$	3s3d $1D$	3s4p $1P^\circ$	3s5s $1S$
Experiment					
Gratton(03) ³⁸	—	46.2 ± 2.6	74.8 ± 3	14.3	101.0 ± 3.5
Chantepie(89) ⁴⁰	2.3	44.0 ± 5	72.0 ± 4	13.4 ± 0.5	102.0 ± 5
Jonsson(84) ⁴¹	—	47.0 ± 3	81.0 ± 6	—	100.0 ± 5
Schaefer(71) ³⁹	—	—	57.0 ± 4	—	163.0 ± 8
Theory					
Fischer(75) ³⁵	2.1	44.8	77.2	13.8	102.0
Chang(86) ³⁶	2.1	45.8	79.5	14.3	100.0
Zheng(01) ³⁷	—	42.3	27.4	—	65.3
QRCC3(G) ^a	2.1	47.03	200	— [*]	99.8
XCC3(G) ^a	2.1	53.8	163.9	14.6	91.9
XCC3(S) ^b	2.1	51.7	79.7	14.1	111.9

^a Gaussian basis set: d-aug-cc-pVQZ^{30,31}

^b Slater basis set: mg-dawtcc5d basis of Lesiuk et al.^{29,32,33}

^{*} Not converged

TABLE V: Lifetimes (ns) of triplet excited states for the Mg atom.

Ref	3s4s $3S$	3s5s $3S$	3s4p $3P$	3s3d $3D$
Experiment				
Aldenius(07) ⁴²	11.5 ± 1.0	29.0 ± 0.3	—	5.9 ± 0.4
Kwiatkowski(80) ⁴³	9.7 ± 0.6	—	—	5.9 ± 0.4
Andersen(72) ⁴⁴	10.1 ± 0.8	—	—	6.6 ± 0.5
Schaefer(71) ³⁹	14.8 ± 0.7	25.6 ± 2.1	—	11.3 ± 0.8
Ueda(82) ⁴⁵	9.9 ± 1.25	—	—	5.93
Havey(77) ⁴⁶	9.7 ± 0.5	—	—	—
Gratton(03) ³⁸	9.8 ± 0.3	25.6 ± 2.1	—	—
Theory				
Fischer(75) ³⁵	9.86	26.8	74.5	6.18
Moccia(88) ⁴⁷	9.7	26.5	81.0	5.8
Victor(76) ⁴⁸	9.07	—	—	6.25
Chang(86) ³⁶	9.98	27.5	77.0	5.89
Mendoza(81) ⁴⁹	9.79	—	—	—
Zheng(01) ³⁷	—	—	78.49	—
XCCSD(S) ^a	12.7	29.87	70.44	5.33

^a Slater basis set: mg-dawtcc5d basis of Lesiuk et al.^{29,32,33}

our result is also within the experimental error of Hunter, Walker, and Weiss⁵¹. In the case of $5s6s^3S$ - $5s5p^3P^\circ$ transition, our result deviates significantly from other theoretical and experimental results. The $5s4d^3D$ - $5s5p^3P^\circ$ transition strengths vary between different

theories and experiments to a large degree. Our result is in reasonable agreement with the latest theoretical result of Porsev *et al.*⁵².

TABLE VI: Transition probabilities (10^6 s^{-1}) of the Sr atom.

Ref	5s6s ¹ S-5s5p ¹ P ^o	5s5p ¹ P ^o -5s4d ¹ D	5s6s ³ S-5s5p ³ P ^o	5s4d ³ D-5s5p ³ P ^o
Experiment				
Hunter(86) ⁵¹	—	0.0039 ± 0.0016	—	—
Jonsson(84) ⁴¹	—	—	66.0 ± 4	—
Brinkmann(69) ⁵³	—	—	91.0 ± 2.5	—
Havey(77) ⁴⁶	—	—	77.0 ± 4.5	—
Borisov(87) ⁵⁴	—	—	—	0.24 ± 0.04
Miller(92) ⁵⁵	—	—	—	0.29 ± 0.03
Theory				
Werij(92) ⁵⁰	18.6	0.0017	71.3	4.32
Vaeck(88) ⁵⁶	—	0.0048	—	—
Porsev(08) ⁵²	—	—	70.9	0.41
XCC3(G) ^a	15.1	0.0027	47	0.70
QRCC3(G) ^a	20.4	— ^o	— [*]	— [*]

^a Gaussian basis set: [8s8p5d4f1g] basis augmented by a set of [1s1p1d1f3g] diffuse functions and the ECP28MDF pseudopotential^{8,30,31,57}

^o Not converged

^{*} Not implemented

D. Possible Hermiticity violation and its consequences

The exact transition moment \mathcal{T}_{LM}^X is Hermitian, i.e., it satisfies the relation given by Eq. (5). This implies that the transition strength \mathcal{S}_{LM}^X , Eq. (3), cannot be negative. This condition is not satisfied in the QRCC theory as well as in the approximate XCC theory. However, in the XCC theory this violation of the Hermiticity originates solely from the truncation of the S operator, while in the QRCC method it has a more fundamental origin. Therefore, the lack of the Hermiticity is expected to be a fairly minor issue in our method, by contrast to the QRCC theory.

For the purpose of this study we investigate some problematic transitions in the Mg atom and Mg₂ molecule which have been encountered beforehand.⁶ We found that the transition strengths for the 3d¹D–3p¹P^o, 3d¹D–4p¹P^o and 3d¹D–5p¹P^o transitions computed with the QRCC code exhibited a non-physical behavior, i.e., some of the contributions were negative. No such artifacts were found in any transition strengths contributions with the

XCC theory. In Table VII we present the differences between \mathcal{T}_{LM}^X and $(\mathcal{T}_{ML}^X)^*$ computed with the QRCC and XCC theories. In QRCC these differences are significant, especially in situations where one is positive and the other is negative. Although in the XCC method the Hermiticity is also violated, we do not observe such strong deviations.

TABLE VII: \mathcal{T}_{LM}^X and $(\mathcal{T}_{ML}^X)^*$ computed with the QRCC and XCC methods for the Mg atom.

Transition	$\mathcal{T}_{LM}^X(\text{QRCC})$	$(\mathcal{T}_{ML}^X)^*(\text{QRCC})$	$\mathcal{T}_{LM}^X(\text{XCC})$	$(\mathcal{T}_{ML}^X)^*(\text{XCC})$
aug-cc-pVQZ				
3s4s 1S - 3s3p $^1P^\circ$	4.3	4.26	4.00	4.01
3s4p $^1P^\circ$ - 3s4s 1S	8.39	8.30	8.36	8.36
d-aug-cc-pVQZ				
3s5s 1S - 3s4p $^1P^\circ$	10.12	10.04	10.08	10.09
3s5s 1S - 3s3p $^1P^\circ$	0.60	0.60	0.51	0.51
3s3d 1D - 3s3p $^1P^\circ$	0.67	-0.4	1.40	1.43
3s4p $^1P^\circ$ - 3s3d 1D	-1.18	0.72	2.64	2.63

A different problem is found for the Mg_2 molecule. In Fig. (2) we present potential energy curves for $(1)^1\Pi_u$, $(2)^1\Pi_u$ and $(1)^1\Sigma_g^+$ states of Mg_2 computed with the EOM-CCSD approximation. We also present a set of transition strengths for various interatomic distances

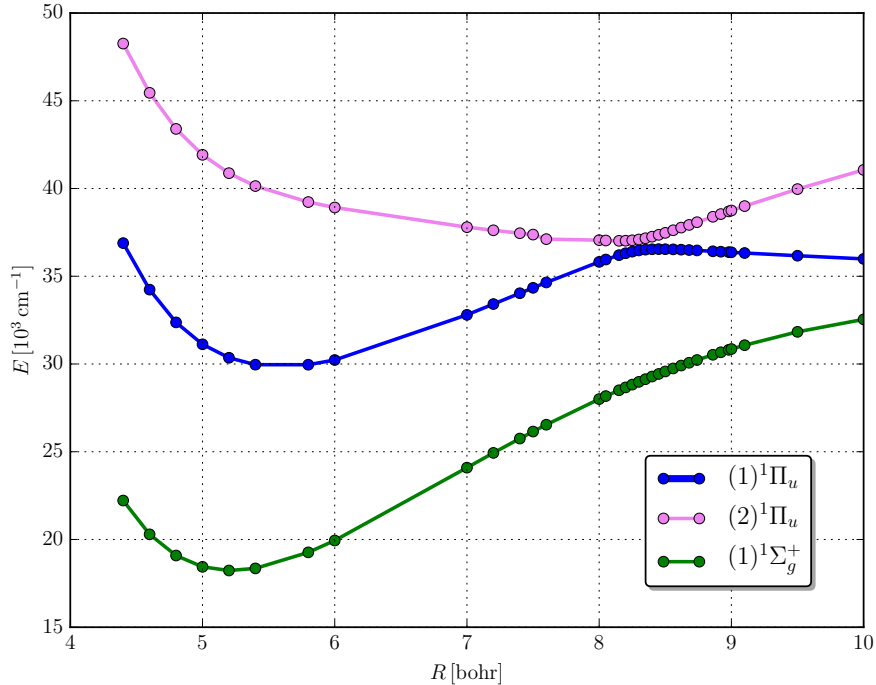


FIG. 2: Potential energy curves for Mg_2 states

R computed with the XCCSD(G) and QRCCSD(G) methods, Fig. (3). For R ranging from 7 to 9 Bohr both methods give similar results. However, the QRCCSD(G) method

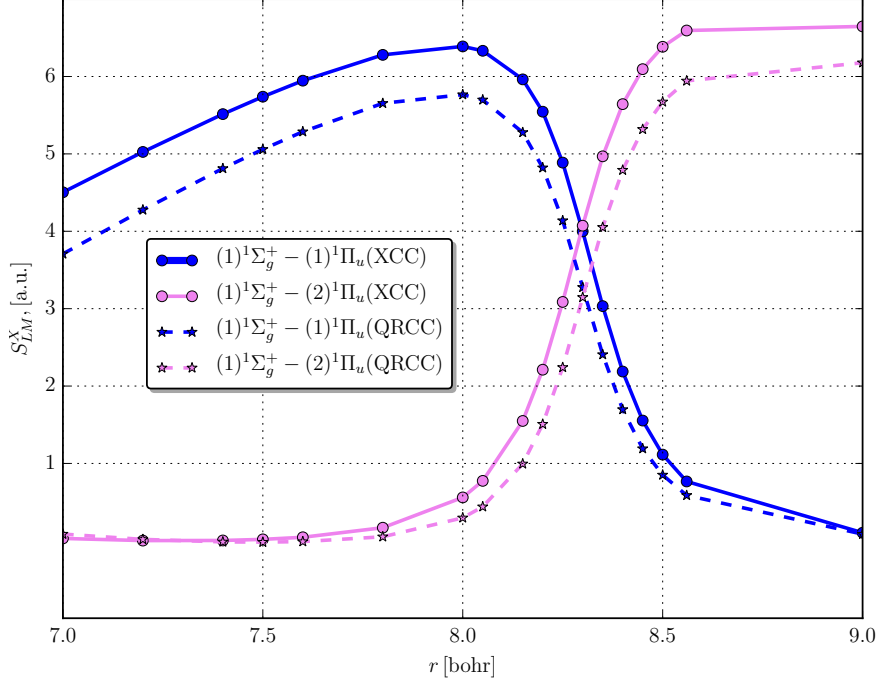


FIG. 3: Transition strengths for Mg_2 computed with XCCSD(G) and QRCCSD(G) method for $R = 7\text{-}9$ a.u.

exhibits problems at small distances where we obtained negative transition strengths that by definition (3) should always be positive. In Fig. (4) we see a pole-like structure which is clearly an artifact, as no such structure should be observed for the transition strengths. By contrast, no such difficulties were found in the XCCSD(G) theory, see Fig. (5). This suggests that the adopted truncation scheme for the S operator has a negligible impact on the behavior of the XCC transition moments.

IV. CONCLUSIONS

We have presented a novel coupled cluster approach to the computation of the transition moments between the excited electronic states. In contrast to the existing CC approaches, our method approximately obeys the Hermiticity relation $(\mathcal{T}_{ML}^X) = (\mathcal{T}_{ML}^X)^*$ and the deviations from this symmetry are negligible. There are three levels of approximations in our formulas for \mathcal{T}_{LM}^X :

1. the underlying model for the CC amplitudes (CCSD/CC3)

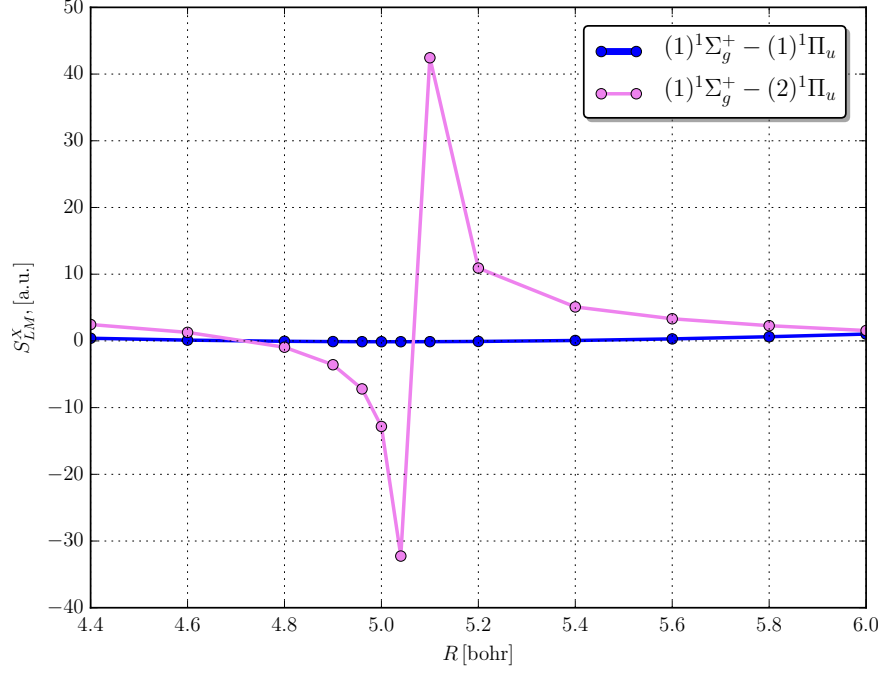


FIG. 4: Transition strengths for Mg_2 computed with QRCC3(G) method

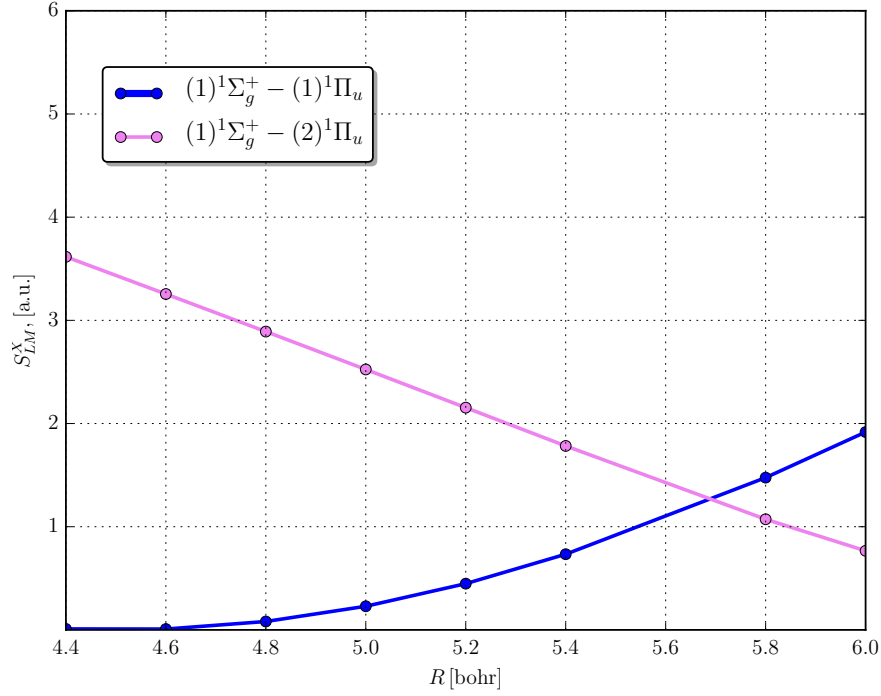


FIG. 5: Transition strengths for Mg_2 computed with XCCSD method

2. approximations of the auxiliary operator S employed in the computation of the expectation values with the CC ground state wave function
3. choice of the commutators included in the expansion of the XCC formula for \mathcal{T}_{LM}^X .

In trouble-free situations, i.e., when the existing QRCC approach satisfies the Hermiticity relation to a good approximation, both methods yield transition moments of a similar quality. However, in certain cases the QRCC method violates the Hermiticity relation to an unacceptable degree and gives unphysical values of the transition strengths. The XCC method does not suffer from this problem. Clearly, this can be viewed as an important improvement over the existing QRCC approach.

We have presented numerical examples for several singlet-singlet and triplet-triplet dipole transitions in the Mg and Sr atoms, and the Mg₂ molecule. Lifetimes derived from the transition moments computed with our method are, in most cases, very close to the available experimental data and to other theoretical results. We have assessed the performance of our method in the STOs basis set and obtained results of significantly better quality than with the available Gaussian basis sets. In certain cases, the use of STOs basis set was the game-changer.

In two the forthcoming papers we will consider calculations of the radial and angular nonadiabatic coupling matrix elements and of the spin-orbit coupling matrix elements between the excited states within the XCC theory. Both works are in preparation.

The code for transition moments between the excited states will be incorporated in the KOŁOS: A general purpose ab initio program for the electronic structure calculation with Slater orbitals, Slater geminals, and Kołos-Wolniewicz functions.

REFERENCES

- ¹D. Zubarev, Usp. Fiz. Nauk **3**, 320 (1960).
- ²J. Linderberg and Y. Öhrn, *Propagators in quantum chemistry* (John Wiley & Sons, 2004).
- ³J. Oddershede, Adv. Chem. Phys. **69**, 201 (1987).
- ⁴L. Rybak, Z. Amitay, S. Amaran, R. Kosloff, M. Tomza, R. Moszynski, and C. P. Koch, Farad. Discuss. **153**, 383 (2011).
- ⁵L. Rybak, S. Amaran, L. Levin, M. Tomza, R. Moszynski, R. Kosloff, C. P. Koch, and Z. Amitay, Phys. Rev. Lett. **107**, 273001 (2011).
- ⁶S. Amaran, R. Kosloff, M. Tomza, W. Skomorowski, F. Pawłowski, R. Moszynski, L. Rybak, L. Levin, Z. Amitay, J. M. Berglund, D. M. Reich, and C. P. Koch, J. Chem. Phys. **139**, 164124 (2013).

- ⁷L. Levin, W. Skomorowski, L. Rybak, R. Kosloff, C. P. Koch, and Z. Amitay, Phys. Rev. Lett. **114**, 233003 (2015).
- ⁸W. Skomorowski, F. Pawłowski, C. P. Koch, and R. Moszynski, J. Chem. Phys. **136**, 194306 (2012).
- ⁹B. McGuyer, M. McDonald, G. Iwata, M. Tarallo, W. Skomorowski, R. Moszynski, and T. Zelevinsky, Nature Phys. **11**, 32 (2015).
- ¹⁰M. McDonald, B. McGuyer, F. Apfelbeck, C.-H. Lee, I. Majewska, R. Moszynski, and T. Zelevinsky, Nature **534**, 122 (2016).
- ¹¹B. McGuyer, C. Osborn, M. McDonald, G. Reinaudi, W. Skomorowski, R. Moszynski, and T. Zelevinsky, Phys. Rev. Lett. **111**, 243003 (2013).
- ¹²B. McGuyer, M. McDonald, G. Iwata, W. Skomorowski, R. Moszynski, and T. Zelevinsky, Phys. Rev. Lett. **115**, 053001 (2015).
- ¹³M. Tomza, M. H. Goerz, M. Musiał, R. Moszynski, and C. P. Koch, Phys. Rev. A **86**, 043424 (2012).
- ¹⁴W. Skomorowski and R. Moszynski, J. Chem. Phys. **134**, 124117 (2011).
- ¹⁵M. Tomza, W. Skomorowski, M. Musiał, R. González-Férez, C. P. Koch, and R. Moszynski, Mol. Phys. **111**, 1781 (2013).
- ¹⁶H. Koch and P. Jørgensen, J. Chem. Phys. **93**, 3333 (1990).
- ¹⁷T. B. Pedersen and H. Koch, J. Chem. Phys. **106**, 8059 (1997).
- ¹⁸G. W. Drake, *Springer Handbook of Atomic, Molecular, and Optical Physics* (Springer, New York, 2006).
- ¹⁹H. Koch, R. Kobayashi, A. S. de Meras, and P. Jørgensen, J. Chem. Phys. **100**, 4393 (1994).
- ²⁰O. Christiansen, P. Jørgensen, and C. Hättig, Int. J. Quant. Chem. **68**, 1 (1998).
- ²¹A. M. Tucholska, M. Modrzejewski, and R. Moszynski, J. Chem. Phys. **141**, 124109 (2014).
- ²²R. Moszynski, P. S. Żuchowski, and B. Jeziorski, Coll. Czech. Chem. Commun **70**, 1109 (2005).
- ²³F. Pawłowski, J. Olsen, and P. Jørgensen, J. Chem. Phys. **142**, 114109 (2015).
- ²⁴B. Jeziorski and R. Moszynski, Int. J. Quant. Chem. **48**, 161 (1993).
- ²⁵H. Koch, O. Christiansen, P. Jørgensen, A. M. Sanchez De Merás, and T. Helgaker, J. Chem. Phys. **106**, 1808 (1997).

- ²⁶T. Korona, M. Przybytek, and B. Jeziorski, *Mol. Phys.* **104**, 2303 (2006).
- ²⁷T. Helgaker, P. Jorgensen, and J. Olsen, *Molecular electronic-structure theory* (Wiley, New York, 2013).
- ²⁸T. H. Dunning Jr, *J. Chem. Phys.* **90**, 1007 (1989).
- ²⁹M. Lesiuk, M. Przybytek, M. Musiał, B. Jeziorski, and R. Moszynski, *Phys. Rev. A* **91**, 012510 (2015).
- ³⁰D. Feller, *J. Comp. Chem.* **17**, 1571 (1996).
- ³¹K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li, and T. L. Windus, *J. Chem. Inf. Model.* **47**, 1045 (2007).
- ³²M. Lesiuk and R. Moszynski, *Phys. Rev. E* **90**, 063318 (2014).
- ³³M. Lesiuk and R. Moszynski, *Phys. Rev. E* **90**, 063319 (2014).
- ³⁴K. Aidas, C. Angeli, K. L. Bak, V. Bakken, R. Bast, L. Boman, O. Christiansen, R. Cimiraglia, S. Coriani, P. Dahle, *et al.*, *WIREs: Comp. Mol. Sci.* **4**, 269 (2014).
- ³⁵C. F. Fischer, *Can. J. Phys.* **53**, 338 (1975).
- ³⁶T. Chang, *Phys. Rev. A* **34**, 4550 (1986).
- ³⁷N. W. Zheng, T. Wang, R. Y. Yang, T. Zhou, D. X. Ma, Y. G. Wu, and H. T. Xu, *At. Data Nucl. Data Tables* **79**, 109 (2001).
- ³⁸R. G. Gratton, E. Carretta, R. Claudi, S. Lucatello, and M. Barbieri, *A & A* **404**, 187 (2003).
- ³⁹A. Schaefer, *Astrophys. J.* **163**, 411 (1971).
- ⁴⁰M. Chantepie, B. Cheron, J. Cojan, J. Landais, B. Laniepce, A. Moudden, and M. Aymar, *J. Phys. B* **22**, 2377 (1989).
- ⁴¹G. Jönsson, C. Levinson, A. Persson, and C.-G. Wahlström, *Z. Phys. A* **316**, 255 (1984).
- ⁴²M. Aldenius, J. D. Tanner, S. Johansson, H. Lundberg, and S. G. Ryan, *A & A* **461**, 767 (2007).
- ⁴³M. Kwiatkowski, U. Teppner, and P. Zimmermann, *Z. Phys. A* **294**, 109 (1980).
- ⁴⁴T. Andersen, L. Molhave, and G. Sorensen, *Astrophys. J.* **178**, 577 (1972).
- ⁴⁵K. Ueda, M. Karasawa, and K. Fukuda, *J. Phys. Soc. Jpn* **51**, 2267 (1982).
- ⁴⁶M. Havey, L. Balling, and J. Wright, *J. Opt. Soc. Am.* **67**, 488 (1977).
- ⁴⁷R. Moccia and P. Spizzo, *J. Phys. B* **21**, 1133 (1988).
- ⁴⁸G. Victor, R. Stewart, and C. Laughlin, *Astrophys. J. Suppl. Ser.* **31**, 237 (1976).
- ⁴⁹C. Mendoza, *J. Phys. B* **14**, 397 (1981).

- ⁵⁰H. Werij, C. H. Greene, C. Theodosiou, and A. Gallagher, Phys. Rev. A **46**, 1248 (1992).
- ⁵¹L. Hunter, W. Walker, and D. Weiss, Phys. Rev. Lett. **56**, 823 (1986).
- ⁵²S. Porsev, A. D. Ludlow, M. M. Boyd, and J. Ye, Phys. Rev. A **78**, 032508 (2008).
- ⁵³U. Brinkmann, J. Goschler, A. Steudel, and H. Walther, Z. Phys. **228**, 427 (1969).
- ⁵⁴E. N. Borisov, P. N. P., and T. P. Redko, Opt. Spectrosc. **63**, 475 (1987).
- ⁵⁵D. Miller, L. You, J. Cooper, and A. Gallagher, Phys. Rev. A **46**, 1303 (1992).
- ⁵⁶N. Vaeck, M. Godefroid, *et al.*, Phys. Rev. A **38**, 2830 (1988).
- ⁵⁷I. S. Lim, H. Stoll, and P. Schwerdtfeger, J. Chem. Phys. **124**, 034107 (2006).